metal-organic compounds

trans-Bis(hinokitiolato)copper(II) trans-bis(hinokitiolato)palladium(II) cocrystals with (5/1) and (3/2) formulations

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trans-Bis(3-isopropyl-7-oxocyclohepta-1,3,5-trien-1-olato)-copper(II) trans-bis(3-isopropyl-7-oxocyclohepta-1,3,5-trien-1-olato)palladium(II) as the (5/1) and (3/2) composites $[Cu(C_{10}H_{11}O_2)_2] \cdot 0.2[Pd(C_{10}H_{11}O_2)_2]$ and $[Cu(C_{10}H_{11}O_2)_2] \cdot 0.67[Pd(C_{10}H_{11}O_2)_2]$, respectively, where 3-isopropyl-7-oxo-cyclohepta-1,3,5-trien-1-olate is the systematic name for the hinokitiolate anion (hino), are the first mixed-metal cocrystal-line products isolated from the M_x(hino)$_y$ family of complexes. These cocrystals contain square-planar trans-Cu(hino)$_2$ and trans-Pd(hino)$_2$ molecules possessing crystallographic inversion symmetry. The bulk formulation for these cocrystalline compounds is $Cu_{1-x}Pd_x$(hino)$_2$, where x is 0.166 (4) for the (5/1) product and 0.399 (4) for the (3/2) product. This bulk formulation is simply a convenient average expression of the whole-molecule substitutional disorder present in these compounds. The $M-O$ bonds are in the range 1.9210 (11)–1.9453 (10) Å, the $O-M-O$ bite angles are in the range 82.94 (4)–83.36 (4)°, and all of the hinokitiolate O atoms are involved in $C-H \cdots O$ hydrogen-bonding interactions.

Comment

Hinokitiol (β-thujaplicin) (Nozoe, 1936) and metal complexes of the hinokitiolate anion, M_x(hino)$_y$, possess a broad range of biological activities, e.g. hinokitiol has antitumor, antibacterial, antifungal and insecticidal properties (Inamori et al., 1993, 2000; Arima et al., 2003; Morita et al., 2003), while its metal complexes exhibit antiviral and antimicrobial properties (Miyamoto et al., 1998; Nomiya et al., 2009). The exact nature of the interactions of these metal complexes with biological targets remains unknown, and even the structural details of the complexes themselves are a relatively recent development. Our own studies have centered on just one of these complexes in particular, i.e. bis(hinokitiolato)copper(II) or Cu(hino)$_2$, in a sustained effort to map out its unusual structural diversity and to provide structural data on the binding interactions that

are available to at least one of these M_x(hino)$_y$ bioactive substances.

$trans$-Cu(hino)$_2$ · $n[trans$-Pd(hino)$_2]$

$n = 0.20$ for (V)
$n = 0.67$ for (VI)
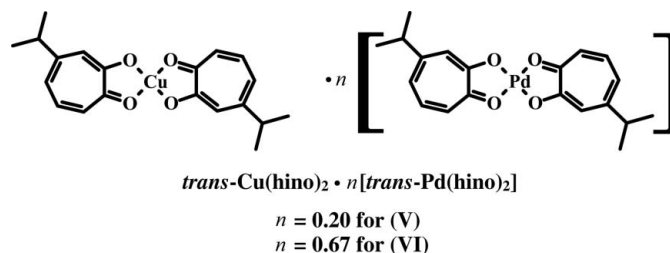
As a brief overview, bis(hinokitiolato)copper(II) is currently known to exist in at least three crystalline modifications, i.e. (I), (II) (Barret et al., 2002) and (III) (Ho, 2010a), with the first of these being polymorphic and existing in four crystalline forms, i.e. (Ia)–(Id) (Barret et al., 2002; Nomiya et al., 2004; Arvanitis et al., 2004; Ho et al., 2009). So far, its structural diversity has been attributed to cis–trans geometric isomerism, syn–anti conformational isomerism, linkage isomerism, aggregation via weak intermolecular $Cu \cdots \pi$ interactions, oligomerization via the hinokitiolate O atoms, and cocrystallization of monomeric, dimeric and trimeric forms of itself with one another. While attachment to a protein or other biological ligand via covalent bonding to the fifth or sixth axial coordination site on the Cu atom is certainly a viable mode of binding, it is also becoming increasingly
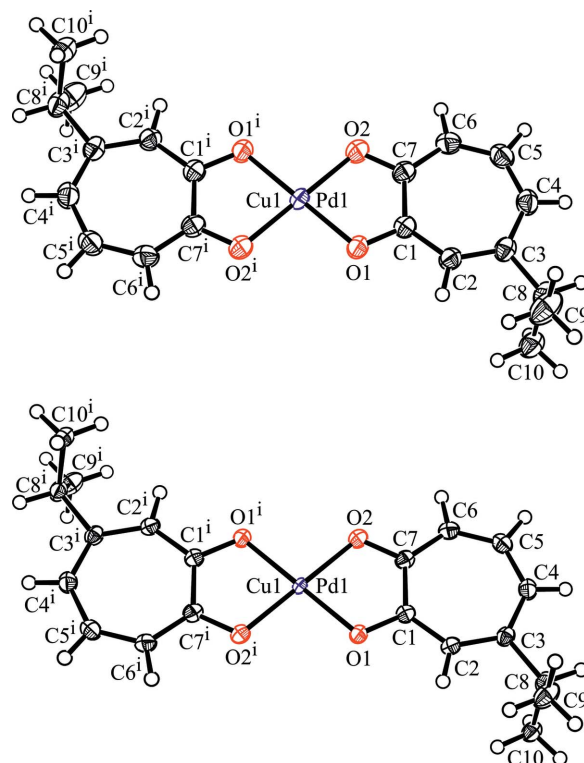
Figure 1
The molecular structures of (V) at 173 K (top) and of (VI) at 100 K (bottom). The metal atoms are depicted as compositionally disordered, i.e. $Cu_{1-x}Pd_x$, where x is 0.166 (4) for (V) and 0.399 (4) for (VI). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x$, $-y$, $-z$.]

evident that the hinokitiolate O atoms possess a propensity for hydrogen-bond interactions that may prove to be competitive or equally important.

Other than $Cu(hino)_2$, the only other four-coordinate square-planar $M_x(hino)_y$ complex that is currently known is bis(hinokitiolato)palladium(II), (IV) (Nomiya *et al.*, 2009). It is therefore only natural to include $Pd(hino)_2$ in any discussion or examination of $Cu(hino)_2$, and to wonder if $Pd(hino)_2$ might also exist in multiple forms. To date, multiple forms of $Pd(hino)_2$ have not been observed, but mixed-metal Cu/Pd cocrystalline products have and are reported herein. Two cocrystalline products were isolated from a mixture of $Cu(hino)_2$ and $Pd(hino)_2$ in diethyl ether that was fractionally crystallized into three batches of crystals. The second batch contained *trans*-$Cu(hino)_2$–*trans*-$Pd(hino)_2$ (5/1), (V), *i.e.* *trans*-$Cu(hino)_2\cdot0.2[trans$-$Pd(hino)_2]$ or $C_{20}H_{22}O_4Cu_{0.83}Pd_{0.17}$. The first batch contained *trans*-$Cu(hino)_2$–*trans*-$Pd(hino)_2$ (3/2), (VI), *i.e.* *trans*-$Cu(hino)_2\cdot0.67[trans$-$Pd(hino)_2]$ or $C_{20}H_{22}O_4Cu_{0.60}Pd_{0.40}$. The third batch contained unincorporated *trans*-$Cu(hino)_2$, (Ia). The general formula for this family of cocrystalline products is $Cu_{1-x}Pd_x(hino)_2$, where x is 0.166 (4) for (V) and 0.399 (4) for (VI). Views of (V) and (VI) are given in Fig. 1, and selected geometric parameters are summarized in Table 1.

As shown in Fig. 1, the mixed-metal cocrystalline products (V) and (VI) are isostructural with each other, with the only obvious visual difference being the larger displacement ellip-

soids for (V) *versus* (VI). This is, of course, simply a reflection of the fact that the data for (V) were collected at 173 (2) K, while the data for (VI) were collected at 100 (2) K. Compounds (V) and (VI) are also isostructural and isomorphous with the previously reported (Ia) (Barret *et al.*, 2002) and (IV) (Nomiya *et al.*, 2009), so a comparison and discussion of some of the key features in all four structures will be made. All four compounds crystallize in the monoclinic space group $P2_1/c$ (No. 14) with their metal atoms located at Wyckoff position 2a. For (V) and (VI), this means that their metal-atom sites are required by symmetry to be compositionally disordered. The $M(hino)_2$ molecules in each structure possess crystallographic inversion symmetry and are planar. The maximum atomic displacements from their respective molecular least-squares planes (excluding the isopropyl atoms) are 0.032 (3) Å for O2 in (Ia), 0.017 (2) Å for O1 in (IV), 0.0254 (11) Å for O2 in (V) and 0.0218 (9) Å for O1 in (VI). The C2—C3—C8—X torsion angles range from −3.32 (16) to −4.6 (6)°, indicating that the full specification for these compounds is $(+sp,-sp)$-*trans*-$M(hino)_2$ (Ho *et al.*, 2009).

A numerical comparison of selected distances and angles for (Ia) and (IV)–(VI) is given in Table 1 and graphically depicted in Fig. 2. The linear increase in the M—O bonds with increasing Pd content (Fig. 2a) is normal. Hence, the observed range of M—O distances [1.900 (2)–1.9797 (26) Å for Δ = 0.08 Å] is in reasonable agreement with the difference in covalent radii for Cu and Pd [1.32 and 1.39 Å, respectively, for
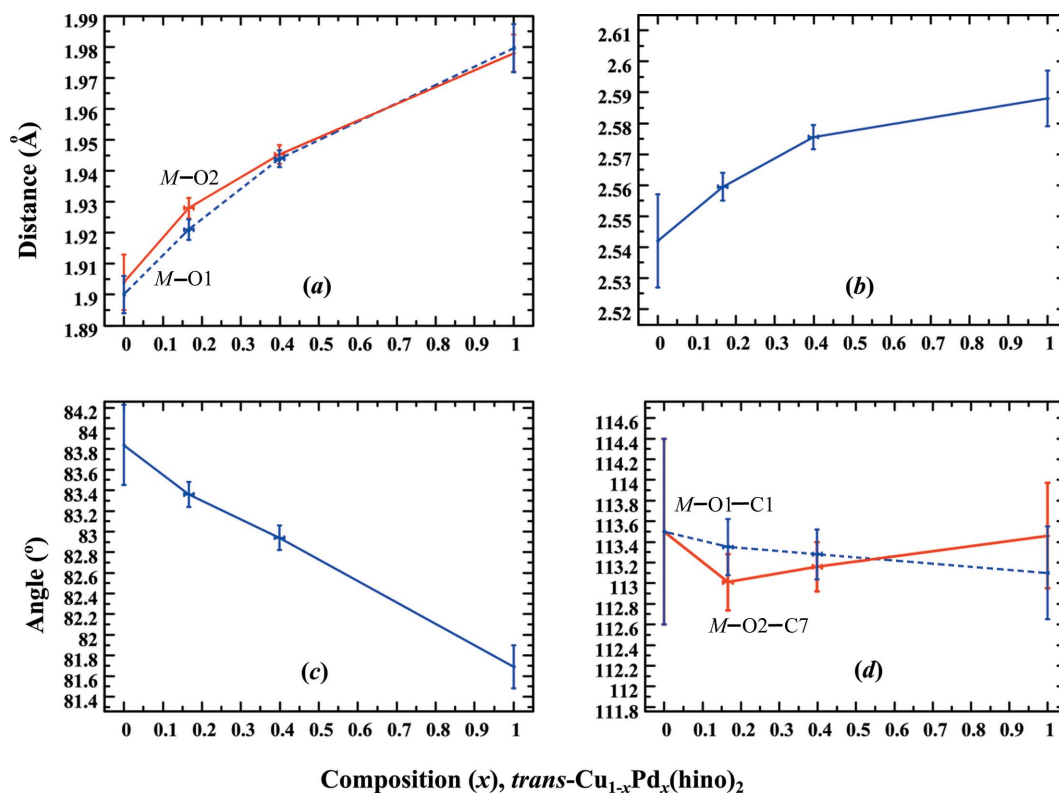

Figure 2
Selected distances and angles as a function of composition: (*a*) M—O1 (dashed line; blue in the electronic version of the paper) and M—O2 (red), (*b*) O1···O2, (*c*) O1—M—O2, and (*d*) M—O1—C1 (dashed line; blue) and M—O2—C7 (red). The error bars depict three standard uncertainties on either side of the refined quantities.

$\Delta = 0.07$ Å (Cordero *et al.*, 2008)], while the intermediate *M*—O values for (V) and (VI) are, of course, the weighted averages of the Cu—O and Pd—O bonds present within those cocrystals. This trend is also observed in the C4···C4^i distances [11.315 (8)–11.474 (5) Å for 2$\Delta = 0.159$ Å or $\Delta = 0.08$ Å, symmetry code: (i) $-x$, $-y$, $-z$], *i.e.* the C4···C4^i distances in this study are primarily a function of composition and atomic radii as well, rather than a function of bowing in the *M*(hino)$_2$ units (Ho, 2010*a,b*). Conversely, a linear decrease in the O—*M*—O bite angle with increasing Pd content is observed (Fig. 2*c*) as would be expected for increasing *M*—O bonds without comparable increases in the C—O distances. The *M*—O—C angles, instead of increasing with increasing Pd content, are surprisingly invariant (Fig. 2*d*). The increase in the O1···O2 distances with increasing Pd content (Fig. 2*b*) is a reflection of why that may be so, *i.e.* the O1—C1—C7 and O2—C7—C1 angles are more strained than the *M*—O1—C1 and *M*—O2—C7 angles upon complexation. As the Pd content increases, that strain is partially relieved by increases in the O1—C1—C7 and O2—C7—C1 angles (see Table 1).

Finally, since the intermolecular interactions were omitted in the earlier descriptions of (I*a*) and (IV), a hydrogen-bonding plot for (VI) is given in Fig. 3 and may be taken to be representative of all four compounds. As shown in Fig. 3, the key feature that was overlooked in the earlier studies is that each hinokitiolate O atom participates in at least one C—H···O interaction resulting in a three-dimensional network of hydrogen bonds in the solid state. The two principal interactions present in (VI) are C5—H5···O1^{ii} [C5—H5 = 0.95 Å, H5···O1^{ii} = 2.39 Å, C5···O1^{ii} = 3.2614 (17) Å and C5—H5···O1^{ii} = 153.0°, symmetry code: (ii) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$] and C8—H8···O2^{iii} [C8—H8 = 1.00 Å, H8···O2^{iii} = 2.50 Å, C8···O2^{iii} = 3.3732 (17) Å and C8—H8···O2^{iii} = 145.2°, symmetry code: (iii) $x + 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$]. The contact distances observed over all four compounds are 2.39–2.50 Å for H5···O1^{ii}, 3.2614 (14)–3.323 (6) Å for C5···O1^{ii}, 2.50–2.57 Å for H8···O2^{iii} and 3.3732 (17)–3.422 (6) Å for C8···O2^{iii}.
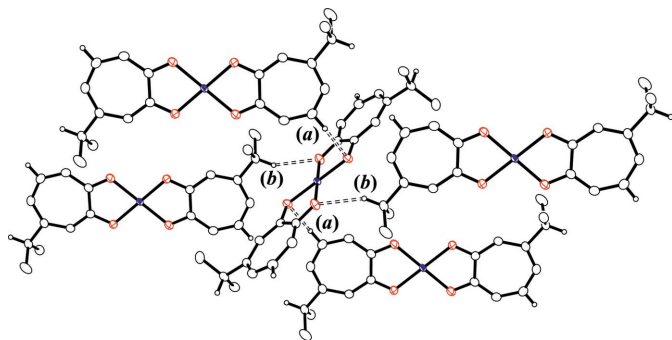

Figure 3
The principal hydrogen-bonding interactions (dashed lines) in (VI). Displacement ellipsoids are drawn at the 50% probability level. The H5 and H8 atoms and their symmetry equivalents are shown as small spheres of arbitrary radii. All other H atoms have been removed, and only the (*a*) C5—H5···O1^{ii} and (*b*) C8—H8···O2^{iii} interactions to the central *M*O$_4$ unit, and their symmetry-related counterparts, are shown for clarity. [Symmetry codes: (ii) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; (iii) $x + 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$.]

These may be compared to the expectation values for aryl C—H···O hydrogen bonds, *i.e.* 2.49 (17)–2.60 (19) Å for H···O and 3.53 (16)–3.63 (19) Å for C···O (Hay & Bryantsev, 2008).

To our knowledge, there are no other reports of mixed-metal cocrystals from the M_x(hino)$_y$ family of compounds or even from the more general M_x(trop)$_y$ class of compounds (where trop is used here to specify any substituted or unsubstituted tropolonate ligand), although such cocrystals must most assuredly exist. Therefore, for a related structure and example, a recently published mixed-metal cocrystal from the M_x(acac)$_y$ family of compounds (where acac is the acetylacetonate ligand) is mentioned, *i.e.* Cu$_{1-x}$Ni$_x$(acac)$_2$ (Shahid *et al.*, 2010). The space group (albeit, using cell choice 2) and disorder treatment used in that example are identical to our own. Shahid and coworkers state that 'in every molecule the [central] position will be occupied by exactly 0.31 Cu and 0.69 Ni atoms'. An alternative interpretation of their occupancy data is that given any three random molecules from their cocrystal, one of those molecules will be Cu(acac)$_2$ and the other two will be Ni(acac)$_2$, *i.e.* theirs is a (1/2) cocrystal. As indicated in the title of our own paper, (V) is a (5/1) cocrystal, *i.e.* given six random molecules, five will be *trans*-Cu(hino)$_2$ and one will be *trans*-Pd(hino)$_2$. Similarly, (VI) is a (3/2) cocrystal, *i.e.* given five random molecules, three will be *trans*-Cu(hino)$_2$ and two will be *trans*-Pd(hino)$_2$. Presumably, a continuum of other (Cu/Pd) ratios may be possible for crystals prepared under other suitable conditions.

In summary, the unique ability of Cu(hino)$_2$ to cocrystallize with different forms of itself as a pathway for structural diversification was previously known. Some of our efforts to understand the range of that coformer ability were presented in this paper. Specifically, *trans*-Cu(hino)$_2$·0.2[*trans*-Pd(hino)$_2$], (V), and *trans*-Cu(hino)$_2$·0.67[*trans*-Pd(hino)$_2$], (VI), have established for the first time that Cu(hino)$_2$ is capable of cocrystallizing with complexes other than itself. These results are significant in that they suggest that other mixed crystalline products (with other metal or even organic compounds) might be possible, a potential route to new M_x(hino)$_y$ formulations with altered or modified biological activities. The structures of (V) and (VI) also provide additional evidence that the hinokitiolate O atoms in these compounds are willing acceptors for hydrogen-bonding interactions, observations that may have a direct bearing on the mode of binding of Cu(hino)$_2$ with biomolecules.

Experimental

Starting materials (II) and (IV) were prepared according to literature procedures (Barret *et al.*, 2002; Nomiya *et al.*, 2009). A mixture of green [*cis*-Cu(hino)$_2$]$_2$·[*trans*-Cu(hino)$_2$]$_2$·*trans*-Cu(hino)$_2$, (II), and red *trans*-Pd(hino)$_2$, (IV), in a 1:1 molar ratio, was dissolved in a minimal volume of diethyl ether. Slow evaporation of the diethyl ether at room temperature was monitored until orange prisms of crystallographic quality and size had grown, at which point the crystals were harvested (batch 1) and the supernatant set aside to evaporate further. The supernatant yielded a second crop of orange prisms (batch 2) and, subsequently, a final crop of green prisms (batch 3). The structures of (V) and (VI) were derived from the intensity

data from crystals from batches 2 and 1, respectively. A data set for a crystal from batch 3 confirmed that the final crop contained unincorporated *trans*-Cu(hino)₂, (I*a*). The presence of both Cu(hino)₂ and Pd(hino)₂ within the crystals of (V) and (VI) was also independently confirmed by ESI–MS using either an Agilent 1100MSD Series Single Quadruple LC/MS or a modified Analytica of Branford ESI with an in-house-built pulsed deflection orthogonal time-of-flight mass spectrometer. Selected *m/z* data for (V): 390, 392 [Cu(hino)₂ + H]⁺; 412, 414 [Cu(hino)₂ + Na]⁺; 429, 431, 432, 433, 435, 437 [Pd-(hino)₂ + H]⁺; 451, 453, 454, 455, 457, 459 [Pd(hino)₂ + Na]⁺. Selected *m/z* data for (VI): 390 [Cu(hino)₂ + H]⁺; 412 [Cu(hino)₂ + Na]⁺; 433 [Pd(hino)₂ + H]⁺; 455 [Pd(hino)₂ + Na]⁺.

Compound (V)

Crystal data

0.83[Cu(C₁₀H₁₁O₂)₂]·· 0.17[Pd(C₁₀H₁₁O₂)₂]
$M_r = 396.99$
Monoclinic, $P2_1/c$
$a = 9.1971 (6)$ Å
$b = 9.8999 (6)$ Å
$c = 11.0409 (7)$ Å

$\beta = 113.2230 (9)°$
$V = 923.83 (10)$ Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.17$ mm⁻¹
$T = 173$ K
$0.17 \times 0.16 \times 0.13$ mm

Data collection

Bruker Kappa APEXII DUO diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
  $T_{min} = 0.830$, $T_{max} = 0.867$

7850 measured reflections
2129 independent reflections
1814 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.062$
$S = 1.04$
2129 reflections

118 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.62$ e Å⁻³
$\Delta\rho_{min} = -0.17$ e Å⁻³

Compound (VI)

Crystal data

0.60[Cu(C₁₀H₁₁O₂)₂]·· 0.40[Pd(C₁₀H₁₁O₂)₂]
$M_r = 407.06$
Monoclinic, $P2_1/c$
$a = 9.1703 (12)$ Å
$b = 9.8475 (12)$ Å
$c = 10.9850 (14)$ Å

$\beta = 112.6809 (19)°$
$V = 915.3 (2)$ Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.14$ mm⁻¹
$T = 100$ K
$0.23 \times 0.08 \times 0.08$ mm

Data collection

Bruker Kappa APEXII DUO diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
  $T_{min} = 0.779$, $T_{max} = 0.918$

8292 measured reflections
2190 independent reflections
1883 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.046$
$S = 1.03$
2190 reflections

118 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.33$ e Å⁻³
$\Delta\rho_{min} = -0.19$ e Å⁻³

Both title structures were solved by molecular replacement, *i.e.* the coordinates for *trans*-Cu(hino)₂, (I*a*), were used as a starting model (Barret *et al.*, 2002). Only the atom labels were changed for consistency with our previously published Cu(hino)₂ structure determina-

Table 1
Selected geometric parameters (Å, °) for *trans*-Cu₁₋ₓPdₓ(hino)₂.

	(I*a*)[a]	(IV)[b]	(V)[c]	(VI)[d]
M—O1	1.900 (2)	1.9797 (26)	1.9210 (11)	1.9439 (9)
M—O2	1.904 (3)	1.978 (2)	1.9280 (11)	1.9453 (10)
O1—C1	1.296 (5)	1.301 (3)	1.3007 (17)	1.3030 (16)
O2—C7	1.293 (5)	1.300 (3)	1.2945 (17)	1.2999 (15)
C4···C4ⁱ	11.315 (8)	11.474 (5)	11.3899 (30)	11.4432 (28)
O1···O2	2.542 (5)	2.588 (3)	2.5595 (15)	2.5756 (13)
O1—M—O2	83.84 (13)	81.69 (7)	83.36 (4)	82.94 (4)
M—O1—C1	113.5 (3)	113.10 (15)	113.35 (9)	113.28 (8)
M—O2—C7	113.5 (3)	113.46 (17)	113.01 (9)	113.16 (8)
O1—C1—C7	114.6 (3)	116.1 (2)	114.82 (12)	115.13 (11)
O2—C7—C1	114.6 (4)	115.7 (2)	115.44 (13)	115.48 (12)
C2—C3—C8—X	−4.6 (6)	−4.3 (4)	−3.48 (19)	−3.32 (16)

Notes: the C2—C3—C8—X values reported are the averages of the C2—C3—C8—C9 and C2—C3—C8—C10 torsion angles for each compound; (*a*) M = Cu1 and x = 0 (Barret *et al.*, 2002); (*b*) M = Pd1 and x = 1 (Nomiya *et al.*, 2009); (*c*) M = Cu1/Pd1 (5/1) and x = 0.166 (4) (this work); (*d*) M = Cu1/Pd1 (3/2) and x = 0.399 (4) (this work); symmetry code: (i) −x, −y, −z.

tions. The metal atoms in these structures are located at Wyckoff position 2*a*, *i.e.* centers of crystallographic inversion symmetry. Their coordinates are therefore invariant and fixed, *e.g.* to (0, 0, 0), and the metal atoms are required to be compositionally disordered, *i.e.* the bulk structures are modelled as having metal atoms of partial Cu and partial Pd character. Hence, during the least-squares refinements, the Cu and Pd atoms were constrained to have equal anisotropic displacement parameters [EADP software command from *SHELXTL* (Sheldrick, 2008)] and their occupancy factors were allowed to vary, yielding compositions of 0.834 (4) Cu and 0.166 (4) Pd for (V), and 0.601 (4) Cu and 0.399 (4) Pd for (VI). These values are in excellent agreement with the calculated values of 0.83 Cu and 0.17 Pd expected for a 5:1 cocrystal of *trans*-Cu(hino)₂ and *trans*-Pd(hino)₂ for (V), and 0.60 Cu and 0.40 Pd for a 3:2 cocrystal for (VI). All of the H atoms were allowed to ride on their respective C atoms, with C—H = 0.95, 1.00 and 0.98 Å for the cycloheptatriene, methine and methyl H atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for the cycloheptatriene and methine H atoms, and $1.5U_{eq}(C)$ for the methyl H atoms.

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* and *SADABS* (Bruker, 2008); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OV3001). Services for accessing these data are described at the back of the journal.

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